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- (71) Applicant: HYBRID PLASTICS [US/US]; 18237 Mount Baldy Circle, Fountain Valley, CA 92708-6117 (US).
- (72) Inventors: LICHTENHAN, Joseph, D.; 18237 Mount Baldy Circle, Fountain Valley, CA 92708-6117 (US). SCHWAB, Joseph, D.; 18237 Mount Baldy Circle, Fountain Valley, CA 92708-6117 (US). AN, Yi-Zong; 18237 Mount Baldy Circle, Fountain Valley, CA 92708-6117 (US). REINERTH, William; 18237 Mount Baldy Circle, Fountain Valley, CA 92708-6117 (US). FEHER, Frank,
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(54) Title: POLYHEDRAL OLIGOMERIC-SILSESQUIOXANES, -SILICATES AND -SILOXANES BEARING RING-STRAINED OLEFINIC FUNCTIONALITIES

(57) Abstract: Processes have been developed for the manufacture of polyhedral oligomeric silsesquioxanes (POSS), polysilsesquioxanes, polyhedral oligomeric silicates (POS), and siloxane molecules bearing reactive ringstrained olefins (e.g. norbornenyl, cyclopentenyl, etc. functionalities). The manufacturing processes employ the silation of siloxides with silane reagents containing at least one reactive ring-strained cyclic olefin functionality or hydrosilation reactions between silanes containing at least one silicon-hydrogen bond with ring-strained cyclic olefin reagents. Each of the processes result in a new chemical species bearing one or more ring strained olefins that can undergo polymerization, grafting, or other desirable chemical reactions to form polymeric products.

Specification

POLYHEDRAL OLIGOMERIC -SILSESQUIOXANES, -SILICATES AND -SILOXANES BEARING RING-STRAINED OLEFINIC FUNCTIONALITIES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to methods of preparing hybrid "organic-inorganic" chemical compositions that are wholly useful by themselves or in combination with other comonomers for producing novel polymeric compositions with desirable physical properties such as adhesion to polymeric, composite and metal surfaces, water repellency, low dielectric constant, resistance to abrasion and fire, biological compatibility, and optical quality plastics. The new compositions reported herein contain two primary material combinations.

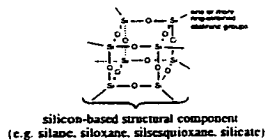


Figure 1. Generic anatomy of invention

Part one of the combination is a silicon component which may be comprised of a silane, silicone, silsesquioxane, polyhedral oligomeric silsesquioxane, silicate, polyhedral oligomeric silicate or combinations thereof. The silicon-component provides chemical oxidation resistance, thermal stability, and structural reinforcement to the overall molecule. The second component of the composition is one or more ring strained olefinic groups. The ring strained olefinic groups provide the primary reactive functionality for polymerization and for solubilization. The ring strained olefin may be comprised in whole or part from primarily olefinic carbon-based rings (e.g. cyclo-propyl, butenyl, pentenyl, hexenyl, norbornenyl). In some cases one or more hetero atoms such as N, O, S, P, B may also be included in the strained olefinic ring (e.g. ring strained cyclic olefinic imides or ethers).

2. Brief Description of the Prior Art

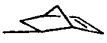

Prior art has demonstrated that strained olefinic rings can be utilized in polymerizations using free radical and UV initiators and transition metal based catalysts. See Haddad et al., J.

1 Amer. Chem. Soc. Polym. Preprints Vol 38, No 1. 1997, pp 127-128, and Mather et. al.
2 Macromolecules Vol 32, (1999), pp 1194-1203 (utility of POSS-polynorbornenes); G. Odian,
3 Principles of Polymerization, 3rd Ed. John Wiley & Sons, (1991) p 578 (polynorbornenes and
4 their utility). Prior art by Tenney et al in USP 5,190,808 described the use of silane-substituted
5 monomers containing only one strained ring olefin, per silicon, for the preparation of preregs
6 for the construction of printed circuit boards. This art was limited in scope and conception and
7 did not fulfill the need for the development of other silicon based strained ring olefin systems
8 that could serve as crosslinkers and zero volatile organic comonomers or as resin systems for use
9 in the manufacture of electronic, medical, sporting goods, aerospace and automotive
10 components, packaging and personal care products. Prior art by Leibfried in USP 4,900,779
11 reported the process of using the hydrosilation of hydridosilanes and strained ring olefins for the
12 purposes of forming crosslinked network materials having tailorable physical properties.
13 Leibfried does not teach methods that allow for the preparation and isolation of silicone, silane,
14 polyhedral oligomeric silsesquioxane or polyhedral oligomeric silicates that bear olefinic
15 strained rings. Nor did they teach the use of such isolable intermediate species for subsequent
16 utility in ROMP polymerizations. Leibfried was also silent as to the usage of silation as method
17 of preparing such materials rather only a hydrosilation method was taught for the attachment of
18 the strained olefinic group to the silane silicon atoms. Literature by Hambley et al. report the
19 preparation of silsesquioxane materials bearing a norbornyl functionality for the purposes of
20 steric bulk and solubility. They did not utilize a strained ring olefinic type of norbornene group
21 and they did not teach the use of such a derivative for polymerization purposes. See Hambley, et
22 al., Applied Organometallic Chemistry (1992) Vol 6 No. 3, pp 253-260.

23 24 SUMMARY OF THE INVENTION

25 It is an objective of this invention to teach the preparation of silicon-based monomers,
26 oligomers, polymers and nanostructures that bear one and more strained ring olefinic
27 functionalities per molecule. When such compositions exist as solids, waxes or oily liquids, they
28 are particularly desirable as low and zero volatility monomers and resins. The viscosity and
29 melting point of such systems can be controlled through the molecular weight, composition and
30 tertiary structure of the molecules. Solid versions of these molecules can exist with crystalline or

1 amorphous solid-state structures. Both forms (solid and liquid) can be utilized as
 2 nanoreinforcements and as fillers in thermoplastics and thermoset systems, while all systems
 3 bearing more than one strained ring olefin can be used as high temperature crosslinkers and
 4 curatives in rubber, silicones, imides, and other olefin based polymers. It is desirable to
 5 incorporate strained ring olefins onto silicone, silsesquioxane, polyhedral oligomeric
 6 silsesquioxane, silicate and polyhedral oligomeric silicate for the purposes of improving
 7 biocompatibility, hardness, fire resistance, oxidation resistance, and mechanical durability.

8 This invention teaches two processes that enable the preparation of strained olefin
 9 bearing silanes, siloxanes, silsesquioxanes, polyhedral oligomeric silsesquioxane, silicates and
 10 polyhedral oligomeric silicate from readily available feedstocks. The preferred manufacturing
 11 processes employ the silation of siloxides (Si-OA , where $\text{A} = \text{H}$, alkaline or alkaline earth
 12 metals) with silane reagents bearing at least one reactive ring-strained cyclic olefin functionality
 13 [e.g., $\text{X}_{3-y}\text{Si}(\text{CH}_3)_y(\text{CH}_2)_2$  where $y = 1-2$ and $\text{X} = \text{OH}$, Cl , Br , I , alkoxide OR , acetate
 14 OOCR , peroxide OOR , amine NR_2 , isocyanate NCO , and R]. Alternatively, the same or closely
 15 related products can be prepared through the hydrosilation reaction between silanes bearing at
 16 least one silicon-hydrogen bond (Si-H) with ring-strained cyclic olefin reagents [e.g., 5-vinyl, 2
 17 norbornene $\text{CH}_2=\text{CH}$ ]. The processes can be effectively practiced using polymeric
 18 silsesquioxanes $[\text{RSiO}_{1.5}]_\infty$ where $\infty = 1-1,000,000$ or higher and which contain unreacted silanol
 19 or silane groups at chain terminus or branch points, on POSS nanostructures of formulas
 20 $[(\text{RSiO}_{1.5})_n]_{\Sigma\#}$, homoleptic, $[(\text{RXSiO}_{1.5})_n]_{\Sigma\#}$, functionalized homoleptic,
 21 $[(\text{RSiO}_{1.5})_m(\text{R}'\text{SiO}_{1.5})_n]_{\Sigma\#}$, heteroleptic, and $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$, functionalized
 22 heteroleptic nanostructures, or on silanes RSiX_3 , or on linear, cyclic, oligomeric and polymeric
 23 siloxanes (polymeric formula $\text{RX}_2\text{Si}(\text{OSiRX})_m\text{-OSiRX}_2$ where $m = 0-1000$, $\text{X} = \text{OH}$, Cl , Br , I ,
 24 alkoxide OR , acetate OOCR , peroxide OOR , amine NR_2 , isocyanate NCO , and R).

25 The advantages of the present invention will become apparent to those skilled in the art
 26 after having read the following detailed description of the preferred embodiment which is
 27 illustrated in the several figures of the drawing.

28

DEFINITION OF FORMULA REPRESENTATIONS FOR NANOSTRUCTURES

For the purposes of understanding this invention's chemical compositions the following definition for formula representations of Polyhedral Oligomeric Silsesquioxane (POSS) and Polyhedral Oligomeric Silicate (POS) nanostructures is made.

Polysilsesquioxanes are materials represented by the formula $[\text{RSiO}_{1.5}]_{\infty}$ where ∞ = molar degree of polymerization and R = organic substituent (H, siloxy, cyclic or linear aliphatic or aromatic groups that may additionally contain reactive functionalities such as alcohols, esters, amines, ketones, olefins, ethers or halides). Polysilsesquioxanes may be either homoleptic or heteroleptic. Homoleptic systems contain only one type of R group while heteroleptic systems contain more than one type of R group.

POSS and POS nanostructure compositions are represented by the formula:

$[(\text{RSiO}_{1.5})_n]_{\sum\#}$ for homoleptic compositions

$[(\text{RSiO}_{1.5})_m(\text{R}'\text{SiO}_{1.5})_n]_{\sum\#}$ for heteroleptic compositions (where $\text{R} \neq \text{R}'$)

$[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\sum\#}$ for functionalized heteroleptic compositions (where R groups can be equivalent or inequivalent)

In all of the above R is the same as defined above and X includes but is not limited to OH, Cl, Br, I, alkoxide (OR), acetate (OOCR), peroxide (OOR), amine (NR_2) isocyanate (NCO), and R. The symbols m and n refer to the stoichiometry of the composition. The symbol \sum indicates that the composition forms a nanostructure and the symbol # refers to the number of silicon atoms contained within the nanostructure. The value for # is usually the sum of m+n. It should be noted that $\sum\#$ is not to be confused as a multiplier for determining stoichiometry, as it merely describes the overall nanostructural characteristics of the system (aka cage size).

IN THE DRAWING

FIG. 1 illustrates the generic anatomy of the invention;

FIG. 2 shows a hydrosilation method for attaching a ROMP group;

FIG. 3 shows a silation method for attaching a ROMP group;

FIG. 4 shows examples of non-nanostructured oligomeric siloxane and silsesquioxane systems;

FIG. 5 shows examples of mono and tris functionalized POSS and POS nanostructure; and

FIG. 6 shows examples of polyfunctionalized POSS, POS, and silsesquioxane resin systems.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention teaches the use of two different chemical processes for the preparation of hybrid (organic-inorganic) silicon-based molecular systems which contain strained organic groups. The process depicted in Figure 2 depicts a general hydrosilation reaction of a POSS-silane with a vinyl or other olefinic group on a molecule that also contains a ring-strained olefinic group. The reaction is effectively carried out with the aid of a late-metal catalyst such as Karsteadts catalyst (at concentration ranges from 0.01 to 5 wt %), Spiers catalyst, and 5% palladium supported on carbon. The hydrosilation reaction effectively promotes the oxidative addition of the silicon-hydride bond from the silane across the olefinic carbon-carbon double bond of the strained-ring olefin bearing compositions claimed herein. The hydrosilation is an effective and reliable process for the addition of strained ring olefins to most silanes, carbosilanes, siloxanes, POSS, and POS systems. The hydrosilation process can produce undesirable isomeric products or impurities that consequently may necessitate purification of the final product to obtain the desired product performance level. The hydrosilation procedure is desirable because of the commercial availability of silicon-based molecules bearing hydride functionalities and vinyl and olefin bearing strained olefinic functionalities.

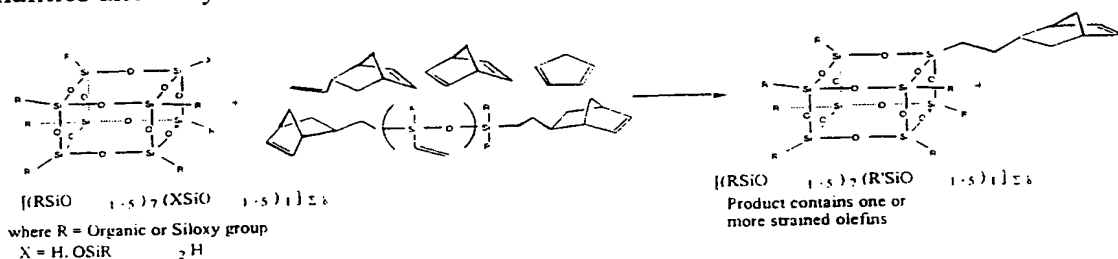


Figure 2: Hydrosilation method for attaching ROMP group. Only monohydrosilation is shown, polyhydrosilations can also be carried out

In cases where the hydrosilation process does not produce satisfactory product compositions or where the method cannot be applied due to the chemical nature of the starting materials, an alternate method of synthesis has been developed. The process in Figure 3 depicts a general silation reaction of a POSS-silanol (or the anionic siloxide equivalent) with a halide (or functional equivalent) silane coupling agent that bears a strained olefinic group. The reaction is desirable because it does not require the use of a metal catalyst and the process is often less exothermic and more selective than the hydrosilation technique. The silation reaction effectively promotes the silation of the silicon atoms in each component through the formation of strong silicon-oxygen-silicon linkages in the desired final product composition. The reaction is also driven by the formation of salts or acidic byproducts that can be removed from the reaction medium using standard trapping, extraction or precipitation methods. The silation procedure is also desirable because of the commercial availability of silicon-based molecules bearing silanol, siloxide, hydroxy, alkoxy groups and silanes bearing strained olefinic functionalities.

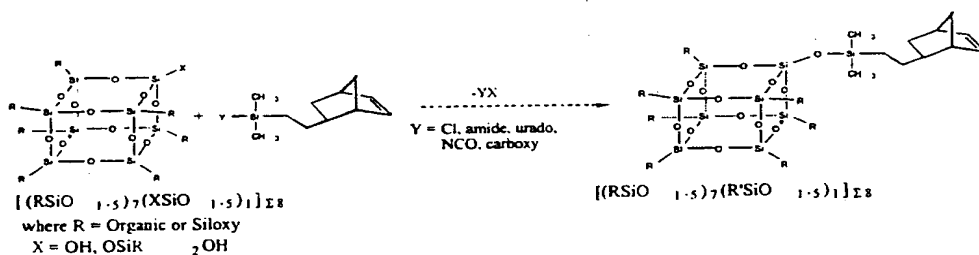


Figure 3. Silation method for attaching ROMP group. Monosilation was shown, polysilations can also be carried out.

Structural representations of specific telechelic compositions that are claimed and which can be prepared using the above procedures are shown in Figure 4. These compositions are in no way limiting and are shown to illustrate the diversity and utility of the described processes.

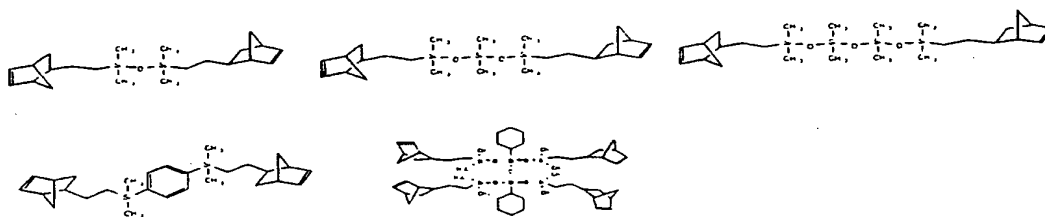
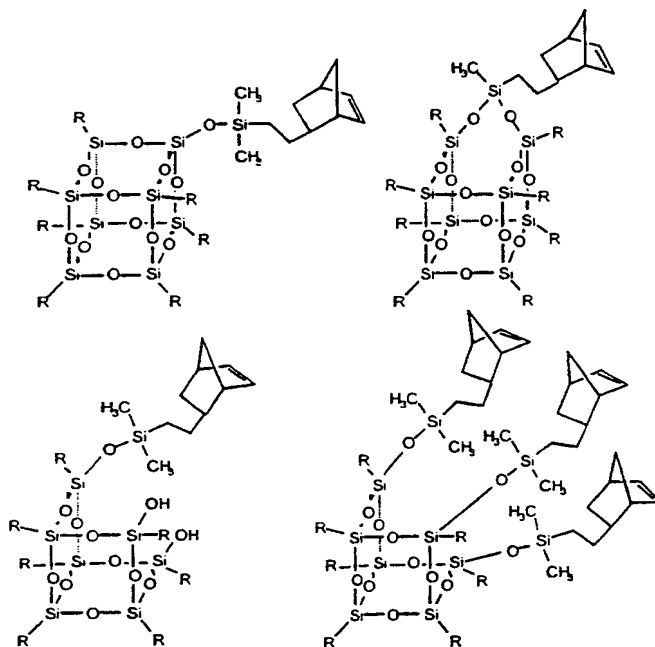


Figure 4. Representative examples of non-nanostructured oligomeric siloxane and silsesquioxane systems

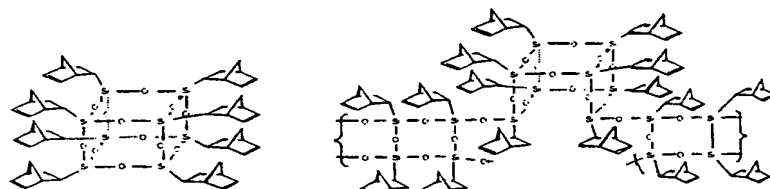
Structural representations of specific POSS and POS compositions that are claimed and which can be prepared using the above procedures are shown in Figure 5. These compositions are in no way limiting and are shown to illustrate the diversity and utility of the described

1 processes. It should further be noted that size of the POSS or POS nanostructure is not a limiting
 2 factor nor does the odd or even number of silicon or heteroatoms contained within a
 3 nanostructure limit the claimed compositions or processes.



4 Figure 5. Examples of mono and tris functionalized POSS and POS nanostructured

5 Structural representations of specific POSS, POS, and silsesquioxane resin compositions
 6 that are claimed and which can be prepared using the above procedures are shown in Figure 6.
 7 These compositions are in no way limiting and are shown to illustrate the diversity and utility of
 8 the described processes. It should again be noted that size of the POSS or POS nanostructure is
 9 not a limiting factor nor does the odd or even number of silicon or heteroatoms contained within
 10 a nanostructure nor the number of strained olefinic groups that can be placed on such a
 11 nanostructure limit the claimed compositions or processes.



12 Figure 6. Examples of polyfunctionalized POSS, POS and Silsesquioxane resin systems

Methods for curing compositions.

All of the compositions can be chemically cured using vulcanizing agents such as organoperoxides, persulfides and sulfur. Examples include AIBN (2,2'-azobisisobutyronitrile), Lupersol™ peroxides, benzoyl peroxide etc. and these are effective in 1-50wt% loadings with loadings of 5-25 wt% being preferred. Such agents will utilize the strained olefinic carbon-carbon double bond as a polymerization point to form inter and intramolecular chemical bonds to adjacent olefinic groups.

The compositions can also be cured using a number of metal-based catalysts such as molybdenum, tungsten, and ruthenium carbenes, halides, phosphates, acetates, and salts. Examples include WCl_6 , $MoCl_5$, (Grubb's catalyst) bis(tricyclohexylphosphine)benzylidene ruthenium (IV), (Schrock's catalyst) 2,6-disopropylphenylimido neophylidenemolybdenum (VI) bis(hexafluoro-t-butoxide), (Feher's catalyst, *see* Feher et al. *J. Am. Chem. Soc.* **1994**, *116*, pp 2145-2146) $[Mo(CHC(CH_3)_2C_6H_5)(N(CH(CH_3)_2)_2C_6H_4)(c-C_6H_{11}SiO_{1.5})_7(c-C_6H_{11}((CH_3)_3SiO)SiO_{0.5})_1]_{\Sigma 7}$ and cocatalysts such as organoaluminum and aluminum halides, such as methyl, ethyl propylaluminum chlorides, bromides and iodides. The catalyst-cocatalysts mixtures utilize ring opening polymerization and ring opening metathesis polymerization to form inter and intramolecular chemical bonds to adjacent olefinic groups. The elimination of ring-strain is a powerful driver of such polymerizations therefore these catalysts are effective at the 0.01 to 1000 millimole per mole of olefin level with preferably loadings of 0.1 to 20 millimole per mol of olefin.

Additionally, the compositions can be cured by reacting them with a number of di and polyfunctional silanes in the presence of a hydrosilation catalyst such as palladium, and platinum halides, olefin complexes or carbon supported versions. Silanes include but are not limited to telechelic hydride terminated oligomers such as tetramethyldisiloxane disilane, polydimethylsiloxane, and nontelechelic hydride bearing systems such as polycarbosilanes, POSS-polysilanes and polysiloxanes. Examples of effective hydrosilation catalysts include Karsteadts catalyst, Spier's catalyst, and 5% palladium supported on carbon. Such catalysts effectively promote the oxidative addition of the silicon-hydride bond of the silane to the olefinic carbon-carbon double bond of the strained-ring olefin bearing compositions claimed herein. The

elimination of ring-strain during the hydrosilation process is also a driver of such polymerizations.

All of the compositions described in this disclosure can be effectively cured using the above methods. Compositions containing two or more strained olefins are particularly effective at increasing the rate of gelation and the extent of cure that can be achieved using the above mentioned procedures. The above mentioned cure techniques can be carried out using common solvents such as hexane, toluene, dichloromethane or they can be conducted without solvents at temperatures sufficient to achieve a molten state. Through compositional formulation with mono, di, tri and polyfunctionalized combinations of the claimed strained olefin bearing compositions, the physical properties, viscosities, and cure times for neat resin mixtures can be selectively tailored to meet individual needs. Cure times ranging from seconds to hours have been achieved.

EXAMPLES

General Process Variables Applicable To All Processes

As is typical with chemical processes, there are a number of variables that can be used to control the purity, selectivity, rate and mechanism of any process. Variables influencing the process for the conversion of polysilsesquioxanes $[\text{RSiO}_{1.5}]_n$ into POSS structures $[(\text{RSiO}_{1.5})_n]_{\Sigma\#}$, $[(\text{RSiO}_{1.5})_m(\text{RSiO}_{1.5})_n]_{\Sigma\#}$, $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$, $[(\text{RSiO}_{1.5})_m(\text{RSiO}_{1.5})_n(\text{RXSiO}_{1.0})_p]_{\Sigma\#}$ include but are not limited to the following: silicon-oxygen ring size, chemical class and composition type $[\text{RSiO}_{1.5}]_n$ (silsesquioxane), $[(\text{RSiO}_{1.5})_n(\text{R}_2\text{SiO})_n]_{\Sigma\#}$ (silsesquioxane-siloxane), $[(\text{RSiO}_{1.5})_m(\text{XSiO}_{1.5})_n]_{\Sigma\#}$ (silsesquioxane-silicate), effect of the organic substituents, process temperature, process solvent, process temperature, stoichiometry and the presence of a catalyst.

Listed below are a series of example processes and compositions which in no way limit the invention. Numerous related compositions and variations to the processes are easily conceived by us and others skilled in the art.

1,4-Bis(ethylnorbornenyldimethylsilyl)benzene. Chloroplatinic acid (0.023 g, 0.044 mmol) was added to a mixture of 1,4-bis(dimethylsilyl)benzene (80 g, 411 mmol) and 5-vinylnorbornene (130 mL, 910 mmol) in toluene (525 mL) at room temperature with magnetic stirring. After about 1.5 h, the solution had become yellow and very hot. A water-cooled condenser was attached and the solution cooled in liquid for 5 min. The cooling bath was removed and the solution allowed to stir at room temperature overnight. After stirring overnight, the solvent was removed in vacuo from the reaction mixture with heating to give a viscous yellow liquid (166.2 g, 93%). Product is a mixture of endo/exo isomers. Data for major isomer is given. ^1H NMR (500 MHz, CDCl_3): δ 7.46 (s, 4H), 6.07 (dd, 2H), 5.84 (dd, 2H), 2.77 (s, 2H), 2.71 (s, 2H), 1.93 (m, 2H), 1.80 (m, 2H), 1.36 (m, 2H), 1.26 (s, 2H), 1.18 (d, 2H), 1.07 (overlapping multiplets, 4H), 0.73 (overlapping multiplets, 4H), 0.44 (m, 2H), 0.21 (s, 6H), 0.20 (s, 6H).

1,5-Bis(ethylnorbornenyl)-1,1,3,3,5,5-hexamethyltrisiloxane. 1,1,3,3,5,5-Hexamethyltrisiloxane (65.7 g, 315 mmol) in toluene (80 mL) was added dropwise over 1.33 h to a mixture of 5-vinylnorbornene (100 mL, 700 mmol) and Karstedt's catalyst (0.050 mL) in toluene (120 mL) at room temperature with magnetic stirring. After the addition had proceeded for about 30 min, the solution had become very hot and so was placed in an ice bath for the remainder of the addition. The addition funnel was rinsed with toluene (25 mL) and this was added to the reaction mixture. After 3 d at room temperature, the solvent was removed in vacuo from the reaction mixture with heating to give a clear, colorless liquid (134.9 g, 95%). Product is a mixture of endo/exo isomers. Data for major isomer is given. ^1H NMR (500 MHz, CDCl_3): δ 6.10 (dd, 2H), 5.90 (dd, 2H), 2.80 (s, 2H), 2.74 (s, 2H), 1.94 (m, 2H), 1.83 (m, 2H), 1.40 (m, 2H), 1.31 (m, 2H), 1.22 (d, 2H), 1.09 (overlapping multiplets, 4H), 0.52 (overlapping multiplets, 4H), 0.04 (s, 12H), 0.01 (s, 6H).

1,7-Bis(ethylnorbornenyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane. 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane (75.3 g, 267 mmol) in toluene (75 mL) was added dropwise over 1.87 h to a mixture of 5-vinylnorbornene (84 mL, 588 mmol) and Karstedt's catalyst (0.050 mL) in toluene (150 mL) at room temperature with magnetic stirring. The addition funnel was rinsed with toluene (25 mL) and this was added to the reaction mixture. After 2 d at room temperature, the solvent was removed in vacuo from the reaction mixture with heating to give a clear,

colorless liquid (120.6 g, 87%). Product is a mixture of endo/exo isomers. Data for major isomer is given. ^1H NMR (500 MHz, CDCl_3): δ 6.10 (dd, 2H), 5.90 (dd, 2H), 2.80 (s, 2H), 2.74 (s, 2H), 1.94 (m, 2H), 1.83 (m, 2H), 1.40 (m, 2H), 1.31 (m, 2H), 1.22 (d, 2H), 1.08 (overlapping multiplets, 4H), 0.53 (overlapping multiplets, 4H), 0.05 (s, 12H), 0.04 (s, 12H).

1,3-Dicyclohexyl-1,1,3,3-tetrakis(ethylnorbornenyldimethylsilyl)disiloxane.

Norbornenylethyldimethylchlorosilane (348 g, 1620 mmol) was added to 1,3-dicyclohexyltetrahydroxydisiloxane (100 g, 326 mmol) and triethylamine (250 mL) in chloroform (700 mL) at room temperature with magnetic stirring. After 4 d at room temperature, the reaction mixture was poured into water and the layers separated. The organic layer was washed with 1N HCl and water and stirred over MgSO_4 and activated carbon. The mixture was filtered through Celite and the solvent was removed from the filtrate in vacuo with heating to give an orange, viscous liquid. Product is a mixture of endo/exo isomers. Data for major isomer is given. ^1H NMR (500 MHz, CDCl_3): δ 6.08 (dd, 4H), 5.87 (dd, 4H), 2.80 (s, 4H), 2.72 (s, 4H), 1.91 (m, 4H), 1.81 (m, 4H), 1.70 (br d, 10H), 1.37 (m, 4H), 1.25 (m, 4H), 1.20 (m, 10H), 1.06 (overlapping multiplets, 12H), 0.48 (overlapping multiplets, 10H), 0.04 (s, 24H). ^{13}C NMR (CDCl_3): δ 136.79, 132.15, 49.53, 44.98, 42.55, 42.33, 32.38, 27.81, 27.09, 26.93, 25.03, 17.31, 0.25, 0.18. ^{29}Si NMR (CDCl_3): δ 7.264, -69.730.

(2-Norbornenylethyldimethylsiloxy)-POSS: 2-Norbornenylethyldimethylchlorosilane

(24.6 g, 0.114 mol, 1.05 eq) was added to a solution of $\text{Cp}_7\text{T}_8(\text{OH})$ (100 g, 0.109 mol) and triethylamine (33.1 g, 45.6 mL, 3 eq) in dry tetrahydrofuran (325 mL). The reaction was carried under an inert atmosphere in a three-necked, 2L-roundbottom flask. Immediately upon addition of the chlorosilane, a precipitate of triethylamine hydrochloride formed. After stirring for 5h an aliquot of the reaction mixture was removed and worked up as described below and analyzed by HPLC. After 5h the reaction is essentially complete. The reaction mixture was transferred to a separatory funnel, the reaction flask rinsed with diethyl ether and the washings added to the contents of the separatory funnel. An additional 200 mL of diethyl ether was added to the flask and the organic phase washed with successive portions of 1N HCl and saturated NaCl solution. The organic THF/Ether phase was dried over MgSO_4 , filtered, and the concentrated by rotary evaporation. The resulting slurry was stirred with methanol and the solid collected by filtration

to provide 105.9 g (89%) of Norbornenylethyldimethylsiloxy-POSS as a white powder. Because the starting 2-Norbornenylethyldimethylchlorosilane contains a mixture of exo and endo isomers, the Norbornenylethyldimethylsiloxy-POSS also contains a mixture of exo and endo isomers. Analysis by HPLC indicates product purity of greater than 99.3%. ¹H NMR spectroscopy (major isomer 91%): 6.09 (1H dd, J = 6 Hz, 3 Hz), 5.90 (1H dd, J = 6 Hz, 3 Hz), 2.79 (br s, 1H), 2.73 (br s, 1H), 1.94 (m, 1H), 1.82 (m, 1H), 1.75 (m, 14H), 1.58-1.50 (m, 44H), 1.38 (m, 1H), 1.21 (d, 1H, J = 8 Hz), 1.07 (m, 2H), 0.98 (m, 7H), 0.57 (m, 2H), 0.47 (m, 1H), 0.08 (s, 6H).

Tris(2-Norbornenylethyldimethylsiloxy)-POSS: 2-

Norbornenylethyldimethylchlorosilane (73.6 g, 0.343 mol, 3.01 eq) was added to a heterogeneous solution of Cp₇T₇(OH)₃ (100 g, 0.114 mol) and triethylamine (57.8 g, 79.6 mL, 0.571 mol 5 eq) in dry tetrahydrofuran (300 mL). The reaction was carried under an inert atmosphere in a three-necked, 2L-roundbottom flask. Upon complete addition of the chlorosilane, the reaction mixture was stirred for 48h. An aliquot of the reaction mixture was removed and worked up as described below. HPLC analysis of the aliquot indicated a single product. The reaction mixture was transferred to a separatory funnel, the reaction flask washed with diethyl ether and the washings added to the contents of the separatory funnel. An additional 200 mL of diethyl ether was added to the flask and the organic phase washed with successive portions of 1N HCl and saturated NaCl. The organic phase was dried over MgSO₄, stirred with activated carbon, and the solvent removed by rotary evaporation. The resulting oil was stirred with MeOH, decanted and dried under vacuum at 70 °C to provide tris(2-Norbornenylethyldimethylsiloxy)-POSS as colorless viscous oil. Because the starting 2-Norbornenylethyldimethylchlorosilane contains a mixture of exo and endo isomers, the Tris(2-Norbornenylethyldimethylsiloxy)-POSS also contains a mixture of exo and endo isomers. Analysis by HPLC indicates a single product. ¹H NMR spectroscopy: 6.09 (3H dd, J = 3 Hz, 6 Hz), 5.90 (3H dd, J = 3Hz, 6 Hz), 2.79 (br s, 3H), 2.73 (br s, 3H), 1.94 (m, 3H), 1.82-1.75 (overlapping multiplets, 17H), 1.58-1.38 (m, 46H), 1.21 (d, 3H), 1.06 (m, 6H), 0.86 (m, 7H), 0.62 (m, 6H), 0.47 (m, 3H), 0.08 (s, 18H).

(2-Norbornenylethyldimethylsiloxy)endodisilanol-POSS: A solution of 2-

Norbornenylethyldimethylchlorosilane (24.5 g, 0.114 mol) in THF (40 mL) was added dropwise

1 to a solution of $\text{Cp}_7\text{T}_7(\text{OH})_3$ (100 g, 0.114 mol) and triethylamine (57.8 g, 79.6 mL, 0.571 mol 5
2 eq) in dry tetrahydrofuran (700 mL). The $\text{Cp}_7\text{T}_7(\text{OH})_3$ /triethylamine solution remained
3 heterogeneous, as all of the $\text{Cp}_7\text{T}_7(\text{OH})_3$ would not dissolve. The addition of the 2-
4 Norbornenylethyldimethylchlorosilane was carried out over a 12h period. Afterwards an aliquot
5 of the reaction mixture was withdrawn and worked up (as described below). HPLC analysis of
6 the product indicated pure (2-Norbornenylethyldimethylsiloxy)endodisilanol-POSS. The
7 reaction mixture was transferred to a separatory funnel and Et_2O (500 mL) added. The organic
8 phase was washed with subsequent portions of 1N HCl (2x150 mL) and saturated brine (1x100
9 mL). The organic phase was dried over anhydrous MgSO_4 and the solvent removed by rotary
10 evaporation to provide (2-Norbornenylethyldimethylsiloxy)endodisilanol-POSS as a white solid.
11 Analysis by HPLC indicates product purity of greater than 99 %. ^1H NMR spectroscopy (major
12 isomer 91%): 6.09 (1H dd, $J = 6\text{Hz}$, 3Hz), 5.90 (1H dd, $J = 6\text{Hz}$, 3Hz), 4.18 and 4.17
13 (overlapping singlets, 2H), 2.79 (br s, 1H), 2.73 (br s, 1H), 1.97 (m, 1H), 1.82-1.75 (overlapping
14 multiplets, 14H), 1.58-1.38 (m, 45H), 1.21 (d, 1H), 1.08-0.98 (overlapping multiplets, 10H),
15 0.62 (m, 2H), 0.47 (m, 1H), 0.120 and 0.116 (overlapping singlets, 6H).

16 **1,3-(2-Norbornenylethyl)1,1,3,3-tetramethyldisiloxane:** A solution of water (6.60 g,
17 0.367 mol, 1 eq) in tetrahydrofuran (60 mL) was added dropwise to a solution of 2-
18 Norbornenylethyldimethylchlorosilane (150 g, 0.698 mol) and triethylamine (204 mL, 148 g
19 1.47 mol, 2.1 eq) in tetrahydrofuran (750 mL). A precipitate of triethylamine hydrochloride
20 formed immediately upon addition of the aqueous tetrahydrofuran. The heterogeneous solution
21 was stirred for 12h, after which an aliquot of the reaction mixture was removed and worked up as
22 described below. Thin layer chromatography (hexane elutant) indicated a single product. The
23 triethylamine hydrochloride was removed by filtration, the filtrate transferred to a separatory
24 funnel and diethyl ether (200 mL) added. The organic phase was washed with 1N HCl and
25 saturated NaCl. The organic phase was dried over MgSO_4 , stirred with activated carbon and
26 filtered. The organic solvent was removed by rotary evaporation to provide 1,3-(2-
27 Norbornenylethyl)1,1,3,3-tetramethyldisiloxane as a pale yellow oil. The final product was
28 purified by vacuum distillation to provide 92 g (70%) of 1,3-(2-Norbornenylethyl)1,1,3,3-
29 tetramethyldisiloxane as a colorless oil. Analysis by ^1H NMR spectroscopy (major isomer 91%):
30 6.11 (1H dd, $J = 6\text{ Hz}$, 3 Hz), 5.90 (1H dd, $J = 6\text{ Hz}$, 3 Hz), 2.80 (br s, 1H), 2.74 (br s, 1H), 1.94

(m, 1H), 1.84 (m, 1H), 1.39 (m, 1H) 1.22 (d, 1H J = 8 Hz), 1.07 (m, 2H), 0.98 (m, 7H), 0.48 (m, 3H), 0.007 (s, 6H).

Preparation of (5-norbornene-2-ethyl)Methylsiloxy Octaisobutyl-POSS: An Et₂O (5 mL) solution of {(i-BuSiO_{1.5})₆(i-Bu(OH)SiO_{1.5})₂}_{Σ8} (890 mg, 1.00 mmol) was added a mixture of Dichloromethyl(5-norbornene-2-ethyl)silane (endo/exo = 3/1, 282.3 mg, 1.20 mmol), Et₃N (195 μL, 1.4 mmol), and Et₂O (5 mL) at -35 °C. After addition the resulting mixture was warmed to room temperature and stirred for 20 h. The mixture was hydrolyzed and extracted with diethyl ether. The organic layer was washed with brine, dried over Na₂SO₄. The residue was passed through a silica gel column using hexane as an eluent. Evaporation of the volatiles gave pure product (720 mg, 0.68 mmol) as a white powder in 68% yield. ¹H NMR (CDCl₃) δ 0.10 (s, 9H), 0.12 (s, 3H), 0.48-0.68 (m, 72H), 0.84-1.05 (m, 194H), 1.06-1.36 (m, 18H), 1.40-1.50 (m, 4H), 1.80-1.94 (m, 32H), 1.95-2.03 (m, 3H), 2.55 (br s, 1H), 2.77 (br s, 3H), 2.78-2.83 (m, 4H), 5.93 (q, ³J = 5 Hz, ³J = 10 Hz, 3H), 6.04 (q, ³J = 5 Hz, ³J = 10 Hz, 1H), 6.09-6.14 (m, 4H). ¹³C NMR (CDCl₃) δ -1.11, 15.86, 16.21, 22.58, 23.20, 23.83, 23.98, 24.06, 24.18, 25.76, 25.81, 25.89, 27.71, 29.50, 32.41, 33.10, 41.89, 41.97, 42.09, 42.65, 45.10, 45.20, 46.03, 49.61, 132.35, 136.29, 136.87, 136.96. ²⁹Si NMR (CDCl₃) δ -69.25, -69.23, -69.21, -69.15, -67.04, -21.73, -21.63. Calcd for C₄₂H₈₈O₁₃Si₉.

Octanorbornenyl-POSS

Norbornenyltriethoxysilane (115 mmoles) reacted with tetraethylammonium hydroxide (115 mmoles) in methyl isobutyl ketone (288 mL) for 72 hours to give norbornenyl-T₈ cage as a white solid (10.65g, 63.9%). ¹H NMR (500.2 MHz, CDCl₃, 300K) δ 6.11 (br), 5.95 (br), 3.00 (br), 2.91 (br), 1.83 (br), 1.77 (br), 1.36 (br), 1.29 (br), 1.17 (br), 1.09 (br), 0.44 (m). ¹³C NMR (125.8 MHz, CDCl₃, 300 K) δ 21.30, 21.32, 21.43, 26.43, 26.79, 26.81, 42.28, 42.30, 42.31, 42.41, 44.23, 46.93, 50.72, 133.78, 133.97, 135.73, 137.63. ²⁹Si NMR (99.4 MHz, CDCl₃, 300 K) δ -68.1, -67.8, -67.5, -67.2, -66.9, -66.7.

1 **Octanorbornenylethyl-POSS**

2 Norbornenylethyltriethoxysilane (115 mmoles) reacted with tetraethylammonium
3 hydroxide (115 mmoles) in methyl isobutyl ketone (288 mL) for 72 hours to give
4 OctanorbornenylethylPOSS cages as a white solid (10.65g, 63.9%).

5 Although the present invention has been described in terms of specific embodiments, it is
6 anticipated that alterations and modifications thereof will become apparent to those skilled in the
7 art. It is therefore intended that the following claims be interpreted as covering all such
8 alterations and modifications as fall within the true spirit and scope of the invention.

9 What is claimed is:

CLAIMS

- 1 1. A process for making oligomeric or polymeric forms of silane, siloxane,
2 silsesquioxane, POSS, silicates, or POS containing at least one strained ring olefin through a
3 hydrosilation process.
- 1 2. A process for making oligomeric or polymeric forms of silane, siloxane,
2 silsesquioxane, POSS, silicates, or POS containing at least one strained ring olefin through a
3 silation process.
- 1 3. Novel compounds comprising silane, siloxane, silsesquioxane, POSS, silicates,
2 or POS containing at least one strained ring olefin.
- 1 4. Novel compounds comprising siloxane telechelics including strained ring
2 functional systems.
- 1 5. Novel compounds comprising silsesquioxane telechelics including strained ring
2 functional systems.
- 1 6. Novel compounds comprising POSS telechelics including strained ring functional
2 systems.
- 1 7. Novel compounds comprising silicate telechelics including strained ring
2 functional systems.
- 1 8. Novel compounds comprising POS telechelics including strained ring functional
2 systems.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/34873

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : CO8G 77/02, 77/04, 77/06, 77/20; CO7F 7/08

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/15, 25, 27, 31, 33, 34, 36, 40, 42; 556/451, 453, 465, 466, 478, 479, 489

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HADDAD, T. S. et al. Hybrid Norbornenyl-Based Polyhedral Oligosilsesquioxane (POSS) Polymers. J. Am. Chem. Soc. Polym. Preprints. January 1997. Vol. 38. No. 1. pages 127-128.	2, 3, 5, 6
X	MATHER, P.T. et al. Mechanical Relaxation and Microstructure of Poly (norbornyl-POSS) Copolymers. Macromolecules. February 1999. Vol. 32. pages 1194-1203, especially page 1195.	2, 3, 5, 6
X	US 3,390,163 A (BROWN et al.) 25 June 1963, col. 1, lines 20-70.	3, 7, 8
X	US 4,381,396 A (RYANG et al.) 26 April 1983, col. 5, lines 17-60.	1, 4



Further documents are listed in the continuation of Box C.



See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	*T* "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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Date of the actual completion of the international search

08 MARCH 2001

Date of mailing of the international search report

04 APR 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ROBERT A. DAWSON

Telephone No. (703) 308-0651

Jean Proctor
Patent Specialist

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/34873

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,657,965 A (WATANABE et al.) 14 April 1987, col. 2, lines 42-68, col. 3, lines 1-5, 36-39.	1, 3, 4
X	US 5,008,360 A (BARD et al.) 16 April 1991, col. 2, lines 44-59, col. 3, lines 5-65.	1, 3, 4
X	US 5,034,490 A (JACOBINE et al.) 23 July 1991, col. 3, lines 15-66, col. 4, lines 5-15.	1, 3, 4
X	US 5,194,489 A (FRANCES et al.) 16 March 1993, col. 2, lines 30-68, col. 3, lines 1-17.	1, 3, 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/34873

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

528/15, 25, 27, 31, 33, 34, 36, 40, 42, 556/451, 453, 465, 466, 478, 479, 489

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

EAST, search terms polysiloxane, organopolysiloxane, polyorganosiloxane, polydiorganosiloxane, diorganopolysiloxane, silicone, silicate, siloxane, silsesquioxane, polysilsesquioxane, strained, ring, norbornenyl, norbornene, norboradiene, cyclopentadiene, silation, silylation, hydrosilation, hydrosilylation, telechelic